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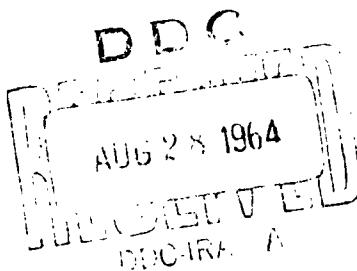
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INTERIM REPORT OF PROGRESS
ON
MARINE CORROSION STUDIES

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METALLURGY DIVISION

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PROBLEM STATUS

Interim report on long term experiments.

AUTHORIZATION

NRL Problem Number M04-02

Bureau Project Numbers SR 007-08-11-2829
SR 007-08-07-1203
WW 041 [R05-24F]
RR 007-08-44-5510

FOREWARD

Corrosion research is characterized by the necessity to conduct experiments that often may extend over a period of many months or even years. Many such experiments may be conducted simultaneously and evaluated at intermediate time intervals, and in some instances the intermediate evaluations may provide the only available guidance at the time in a given problem area.

The interim progress report system has, therefore, been initiated to make available the information derived from incompletely completed studies. Every task will not be reported in each interim but rather only those tasks on which significant findings become available. Additionally, brief communications may be included to report work that does not appear to warrant a separate topical report. The results of major tasks, when completed, will be summarized in separate topical reports.

It should be emphasized that the conclusions reached at an intermediate stage of a study are preliminary and may well have to be modified during the remaining course of the study.

I. CATHODIC PROTECTION STUDIES

A. CORROSION PROTECTION OF O-RING SEALS FOR MARINE SERVICE

Prepared by B. F. Brown

SR 007-08-11-2829

O-ring seals are being used for water-tight closures on various deep-sea devices, such as instrument packages. There are at this time no uniform standards for these seals. The recommendations of O-ring manufacturers regarding groove dimensions and surface finish for high vacuum equipment have been used by several contractors for deep sea equipment and appear to afford good sealing action.

Although the crevice between the mating flanges of an O-ring seal is extremely small, and diffusion of corrodent down it would be expected to be slow, it was thought desirable to examine the corrosion aspects of O-ring seals experimentally in view of the anticipated widespread use of such seals.

Six highly stylized O-ring flange units were prepared using commercial O-rings which will be designated as made of material V. Only one of each pair of mating flanges was of metal, the other being of heavy (1-inch thick) methyl methacrylate in order to permit viewing the progress of corrosion. The metals used were mild steel, AISI Type 304 stainless steel, and 90-10 cupronickel.

Each flange was 4-inches in diameter. The O-ring grooves were located eccentric with respect to the flange, as it was thought of possible interest to be able to observe the inward progress of corrosion even after corrosion had reached that part of the O-ring closest to the flange edge. At the closest point there was about a 3/4-inch distance between the O-ring and the edge of the flange. The flange units were made in duplicate in order that one with each metal could be evaluated without cathodic protection and one with a zinc anode bolted to the back face of the metal flange.

Inside the O-ring a small well was machined in which were placed several grains of commercial indicating calcium sulfate type desiccant. The indicator began to change color slowly during the several weeks between assembly and immersion. This is attributed tentatively to moisture adsorbed on the surfaces of the metal and the plastic since similar specimens made later to the same specifications, except carefully vacuum-dried, did not show a color change in the indicator.

The specimens were immersed for 3-1/2 months in flowing full-salt seawater (78-80°F) which was pumped from the ocean at Fort Amador (Canal Zone) through an all-plastic system. Flanges were examined intermittently without disassembly during the exposure period. After removal from exposure they were returned to NRL for photography (Fig. I-A-1), disassembly, and detailed examination.

The small numbers on the plastic faces in Fig. I-A-1 identify the specimens: 1 and 2, cupronickel; 3 and 4, stainless steel; 5 and 6, plain carbon steel. The even numbered specimens had the zinc anodes on the back and therefore could possibly receive cathodic protection. The odd numbered O-ring flange units did not have cathodic protection.

Corrosion clearly shows in the well of specimen [5], but not in [6]. Upon disassembly of [5], rust was observed where the O-ring contacts the steel, but this was not observed in [6] which had a zinc anode attached.

The unprotected stainless steel [3] was actively corroding over the entire face of the flange, especially near the O-ring, but this had not yet undermined the O-ring. No crevice corrosion was observed on the cathodically protected stainless steel [4].

The unprotected cupronickel [1] was lightly corroded in the crevice but this had not undermined the O-ring. The cupronickel specimen coupled to zinc [2] was much more lightly corroded than the unprotected one, but it, too, was undergoing a reaction, in the crevice between the flanges, which is properly designated as corrosion rather than mere staining.

From experience with cathodically protecting condenser tubes one would not be optimistic about protecting a deep narrow crevice against corrosion. It is clear from

Fig. I-A-1, however, that galvanic anodes can be highly effective for flanges, in which the corrodent in the crevices is not being continuously renewed as it is in condenser tubes.

Long-term experiments with stainless steel Types 304 and 321 are already underway, employing an arrangement similar to that of Fig. I-A-1. These are intended to see whether eventually the O-rings will be undercut by corrosion of the stainless steel in the absence of cathodic protection. Still further tests employing other materials are in various stages of planning and execution.

Until and unless evidence to the contrary appears, it would appear advisable to apply cathodic protection to O-ring seals, particularly if these are made of carbon steel or stainless steel.

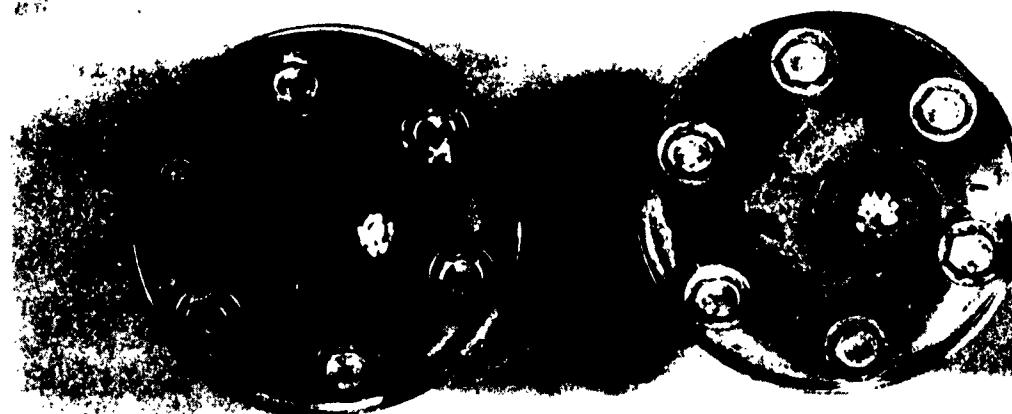
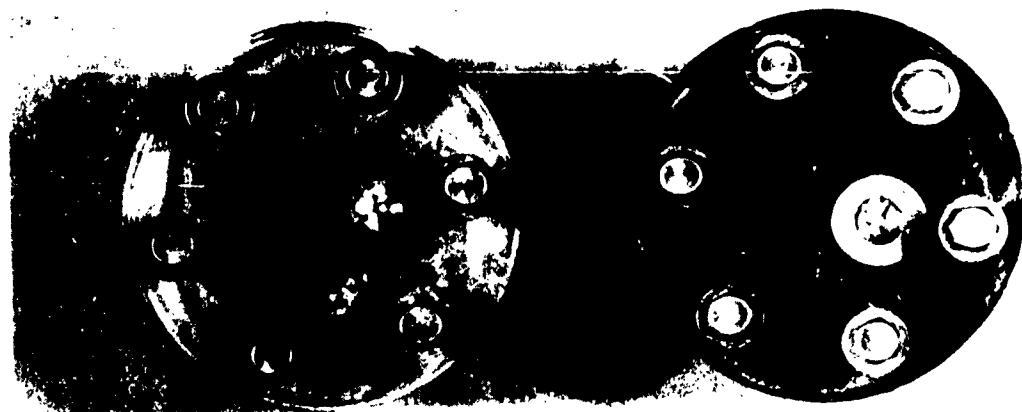
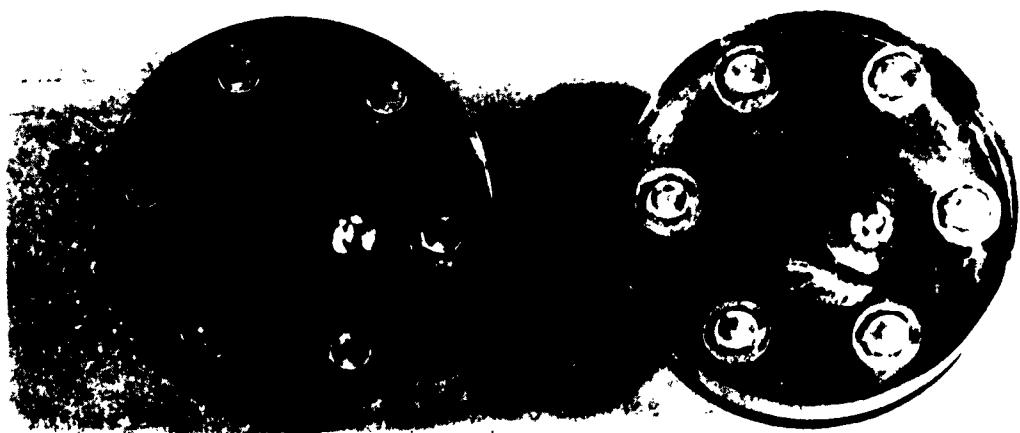


Figure I-A-1

B. CATHODIC PROTECTION OF THE U. S. COAST GUARD VESSEL
"SALVIA"

Prepared by L. J. Waldron

SR 007-08-07-1203

The "SALVIA" was inspected on 15-16 April 1964 while in drydock at Mobile, Alabama, and reported on in detail in NRL Technical Memorandum 6320-36 of 4 May 1964, entitled "Inspection of the Hull and Cathodic Protection System on the U. S. Coast Guard Ship 'SALVIA'". This vessel had been fitted with an aluminum-alloy anode system of cathodic protection while undergoing overhaul in November 1962 at Curtis Bay, Maryland. Individual anodes measured 6" x 12" x 1-1/4" and had a cast-in steel strap containing two drilled holes that fitted over metal studs welded to the bilge keels. A lock-washer and nut served to secure the anode tightly to the hull.

Twenty anodes were mounted on each side of the hull (total of 40 anodes) flush against the painted bilge keel. These aluminum alloy anodes were furnished by the U. S. Naval Research Laboratory for the purpose of evaluating their effectiveness and practicability for the cathodic protection of this painted-steel hull against corrosion.

All anodes were completely covered with rather adherent corrosion products. It was estimated that they had lost approximately 30% of their original weight. The aluminum-alloy anodes had rendered satisfactory protection to the forward one-half of the hull but had failed to provide

adequate protection against corrosion on the aft portion of the hull. Lack of adequate protection was particularly evident on the rudder skeg, keel areas adjacent to the skeg and the two steel fairwaters fore and aft of the propellers.

Four of the anodes were returned to NRL for further study. Preliminary weight loss measurements on one anode indicate that an average current of almost one-quarter of an ampere was obtained per anode or a total average current of about 10 amperes from all anodes during the 16-1/2 months the vessel was in the water.

The appearance of the one anode cleaned of corrosion products for the weight loss determination indicated uniform anode consumption. Additional work has been carried out on four anodes that were removed from the hull to determine the characteristics of the corrosion products. No evidence was found that these products reduced the current that would normally flow from the anode to the hull.

The appearance of the hull and small amount of anode consumption leads to the conclusion that the anode system furnished insufficient current for adequate protection of the hull. Considerably more current apparently was required for polarization with the cold plastic paint used than has been observed with similar hulls coated with standard Navy vinyl systems. In addition, this vessel apparently operated for a considerable portion of the time in fresh to brackish water and this could have contributed to the low current output of the anodes.

C. CATHODIC PROTECTION OF RESERVE FLEET VESSELS AT SAN DIEGO GROUP, PACIFIC RESERVE FLEET

Prepared by L. J. Waldron

SR 007-08-07-1203

The San Diego Group, Pacific Reserve Fleet was visited from 30 March to 3 April 1964 at the request of the Bureau of Ships. This visit was made to observe the performance of cathodic protection, to evaluate the performance of automatic potential control, and to determine the cause of automatic controllers inability to maintain preferred potentials on some of their vessels. In addition, the hulls of two vessels that had been under cathodic protection for approximately 8 years, were inspected while in drydock. All of the above items were reported in detail in NRL Technical Memorandum 6320-38 of April 1964, entitled "Trip Report on Cathodic Protection at the San Diego Group, Pacific Reserve Fleet".

The results of this trip are summarized below:

1. Effect of Water Conditions on Potentials. San Diego Harbor has for many years had a peculiar water condition with regard to cathodic protection. This has been attributed to a cycling effect or an imbalance in the biological characteristics of the water. This causes rapid depolarization of steel surfaces that are receiving cathodic protection currents.

Because of the water fluctuations and imbalance it has been very difficult to maintain potentials entirely within

the specified ranges. Consequently the inspection people of the Group have been rendering unsatisfactory reports on cathodic protection. It was suggested that occasional potential readings slightly below the specified ranges should not be reasons for classing their cathodic protection as unsatisfactory. The imbalance in the water at San Diego will be an item of concern for some time to come when cathodic protection systems are being evaluated.

2. Automatic Control. Inspection of the automatic control systems at the San Diego Reserve Fleet indicates they have been partially successful. Two of the three controllers have operated successfully but are not presently entirely satisfactory because of the increased current demands of the various hulls under cathodic protection.

The saturable reactor type of controller furnished by NRL has been returned to NRL for check and placement in an operating condition. Further tests of the electro-mechanical and saturable reactor types of controllers are planned.

3. Examination of the Hulls of Two Vessels After Approximately Eight Years of Cathodic Protection. Cathodic protection was judged to have been very effective in maintaining a rather excellent condition of the hulls of these two vessels. This was true in spite of the fact that most of the paint (estimated at 80%) had become badly deteriorated. In addition, hull potentials were slightly below the minimum specified level during considerable periods. The relatively

poor conditions of the hull paint undoubtedly accounted for the exceedingly high values of current (approximately 100 amps) required for each hull. These observations should be given considerable future emphasis since Reserve Fleet vessels remain out of dock for longer and longer periods without hull coatings being renewed.

4. Lead-Silver Anodes. The lead-2% silver anodes that are presently being used are giving fairly good performance, but premature failures are much greater than they should be. These failures are caused in part, it is believed, by the inspection teams who take the weekly potential readings. During the inspections, each anode is apparently pulled out of the water for visual examination. In the process, anodes are also shaken back and forth to remove sea growth adhering to either the anode or lead wire.

Severe flexing of the rod-shaped lead anodes tends to loosen and flake off the heavy protective oxide coating that forms on the anode. Once this coating is removed further metal is consumed in forming a new coating when current is passed from the anode. Continual flexing and removal of the coating will eventually lead to accelerated anode consumption and result in breaking of the rod. Anode replacement is then required prematurely. It was recommended that this procedure be eliminated and that all anodes be handled without shaking or flexing.

5. General. While at the San Diego Group, a general talk on the theory, principles, and practical operation of cathodic protection was given to Group personnel.

D. ALUMINUM BASED ANODES

Prepared by M. H. Peterson and
L. J. Waldron

SR 007-08-07-1203

1. Introduction:

In the past decade there has been an increasing interest in the use of aluminum based alloys as galvanic anodes for the cathodic protection of marine structures. In addition to the use of such anodes as a substitute for zinc anodes on structures such as instrument cases and submarine hulls which are weight-limited, there could be a considerable economic advantage if the high theoretical ampere-hour per pound output of aluminum anodes could be realized in practice. At the beginning of the decade, the aluminum anodes available exhibited a maximum electrochemical efficiency of thirty-five percent, or an output of approximately 400 ampere-hours per pound. At this electrochemical efficiency, the weight advantage of aluminum anodes over zinc is slight, and aluminum anodes are at a considerable economic disadvantage.

The electrochemical efficiencies of commercially available aluminum anodes has gradually increased until anodes are available with a claimed efficiency of 80%, or an output of 1000 ampere-hours per pound. However, there has been considerable discrepancy between electrochemical efficiencies

as determined in the laboratory by aluminum anode producers and those determined using full size anodes under conditions simulating the field use of the anode. In the work reported herein, an effort has been made to determine the efficiencies of the anodes under conditions essentially identical with those associated with the use of the anodes for cathodic protection.

2. Experimental Details:

a. Test Site. The test site utilized for this work is located at Portsmouth, Virginia on the Elizabeth River near its merger with the James River. At this site a sea wall about 1500 feet long and composed of interlocking steel piling is available for use as a cathode. The individual piles are about 30-40 feet in height, with one-third of the pile in the bottom mud, one-third in clear water, and one-third exposed to marine atmosphere. Electrical continuity along the length of the sea wall has been assured by welding a one-inch bead at each juncture of the individual piles. The water resistivity varies seasonally between 30 and 100 ohm-centimeters.

b. Procedure. The anodes in the experiment were suspended from steel supports along the sea wall at 40-foot intervals. A single-conductor number 6 cable was used both for hanging the anodes and as an electrical conductor. The total ampere-hour output of each anode was

measured with an accumulative ampere-hour meter that had a rated absolute accuracy of 2%. The meters were read weekly to insure continuous operation. Any errors, however, were non-cumulative and the final readings were used in the computation of the electrochemical efficiency. The total metallic resistance was measured with a low-resistance ohmmeter and the values obtained were always below 0.05 ohm. These measurements included meter resistance, lead-wire resistance, and contact resistance.

3. Experimental Results:

A summary of the electrochemical efficiency, the 95% confidence limit for ampere-hours per pound output, and the mean current density for each type and size of aluminum anode investigated during the past several years is shown in Table I-D-1. The 95% confidence limit for the mean value of the output in ampere hours per pound is the best estimate from the data available. The rather large variation in the value of the confidence limits reflects the fact that many more anodes of some compositions were investigated than was true for the compositions of least interest. The cumulative value of the efficiency and the 95% confidence limit for ampere-hour per pound output of magnesium and zinc anodes are also included for comparison. The ampere-hour per pound output for magnesium and zinc anodes

represent mean values of experiments conducted over a number of years.

The composition of the aluminum alloy anodes used in these experiments are shown in Table I-D-2. Types A-1-A and A-1-B and Type R-4 anodes were proprietary compositions and the manufacturer have asked that the composition not be published. Current production aluminum anodes in general use conform closely to the composition limits shown by Types A-1-A and A-1-B.

Type R-5 is an experimental anode containing extremely low impurity levels. All elements other than aluminum and zinc are maintained at a total level of less than 0.01%. It is not known if production anodes can be sold competitively and this level of purity maintained.

4. Summary and Conclusions:

It is evident that aluminum anodes are now available in production lots which will deliver about 1000 ampere-hours per pound output. It is also evident that anodes with this performance are not limited to one composition or casting practice. One thousand ampere-hour per pound aluminum anodes may be obtained by several avenues of approach.

Any attempt to generalize however, as to the reason for the improved electrochemical efficiency, or for the failure of some anode types to yield high electrochemical efficiencies, is very difficult.

Nevertheless, some general conclusions may be drawn. The belief in the industry that efficiency is improved by maintaining the iron level as low as is practicable has been supported by these experiments. Anode Type R-5 with a very low impurity content showed the highest ampere-hour per pound output of any anode type under test; proprietary anodes A-1-A and A-1-B are also low iron anodes. The high iron content anodes (Type R-2) were clearly much inferior to any other anode type and the Type R-1-B was inferior to the lower iron R-1-A.

Factors other than electrochemical efficiency must be considered in selecting alloy compositions for galvanic anodes. For example, anode Type R-4 with a reasonably high electrochemical efficiency had a driving voltage so low that it would be of doubtful use for cathodic protection of steel. All other aluminum anodes had suitable driving voltages, but variations were noted between proprietary and non-proprietary materials.

It is believed that aluminum anode alloy development has reached a state where, for some specific applications, they are clearly superior to zinc anodes. Increased reliability, mainly less lot-to-lot variation, would make aluminum anodes economically very attractive for general external marine use.

As a precautionary measure, the U. S. Coast Guard should be consulted as to current regulations concerning the sparking hazard before aluminum anodes are considered for tanks which alternately carry ballast and petroleum products. The sparking hazard may result either from a completely dislodged anode or pieces of aluminum dislodged from a partially expended-in-service anode striking the tanks rusted surfaces. Except for the above, aluminum anodes may generally be used interchangeably with zinc anodes.

TABLE I-D-1
COMBINED ALUMINUM ANODE TESTS

<u>Anode Type</u>	<u>Nominal Size</u>	<u>Mean Current Density (ma/sq in.)</u>	<u>Efficiency (%)</u>	<u>95% Confidence Limits for Ampere-Hours/lb.</u>
A-1-A	6"x12"x1 $\frac{1}{4}$ "	4.8	70	890 \pm 35
A-1-B	6"x12"x1 $\frac{1}{4}$ "	4.4	77	990 \pm 65
R-1-A	1 $\frac{1}{2}$ "x1 $\frac{1}{2}$ "x40"	5.3	47	610 \pm 50
R-1-B	3"x4"x20"	2.3	31	405 \pm 35
R-2	3"x4"x20"	1.9	24	310 \pm 30
R-3	6"x12"x1 $\frac{1}{4}$ "	4.0	42	540 \pm 160
R-4	6"x12"x1 $\frac{1}{4}$ "	3.5	67	895 \pm 117
R-5	6"x12"x1 $\frac{1}{4}$ "	4.6	82	1065 \pm 95
Mg			61	615 \pm 12
Zn			96	356 \pm 2

TABLE I-D-2
COMPOSITION OF ALUMINUM ANODES

<u>Anode Type</u>	<u>% Zn</u>	<u>% Fe</u>	<u>% Si</u>	<u>% Sn</u>
[A-1-A] A-1-B		-----Proprietary-----		
R-1-A	6.2	0.10	0.08	-
R-1-B	5.5	0.16	0.08	-
R-2	4.0-6.1	0.65-0.75	0.12	-
R-3	7.5	0.05	0.05	0.13
R-4		-----Proprietary-----		
R-5	5.5	All other impurities total less than 0.01%		

E. STATUS REPORT ON THE CATHODIC PROTECTION OF WIRE ROPE

Prepared by M. H. Peterson

SR 007-08-11-2829

1. Introduction:

There is a definite need for an economical and reliable rope suspension system for use in deep ocean moors, instrumentation systems, and a reliable long-life high-strength armor for cables. One possible solution to the problem is the use of conventional wire rope or metallic armor with a supplementary cathodic protection system to reduce or prevent corrosion. There is, however, no reliable information as to the length of wire rope or armor which can be protected by a unit galvanic anode installation. This has an important bearing on the problem as it may very well be practical to install anodes at 500 or 1000-foot intervals while it would clearly be impractical to install anodes at 50-foot intervals on a 15,000-foot line.

2. Experimental Details:

As part of a continuing study of this problem, long lengths of several types of wire ropes, both unprotected and cathodically protected, were exposed in sea water at Rodman (Pacific entrance to the Panama Canal). Three-sixteenths-inch diameter ropes of bright improved-plow-steel, galvanized improved-plow-steel, monel, and Type 304 stainless steel were used in the experiment.

Exposure began on 10 December 1963. At that time 30-foot lengths of each of the materials in an unprotected condition were exposed as controls. Longer specimens with a nominal length of 450 feet and a zinc anode installed at one end were exposed to evaluate the effect of cathodic protection and to determine if possible the length of rope which could be protected by a single anode. The experiment with bright improved plow steel was terminated on 20 February 1964, while the experiments with the other materials continue.

3. Experimental Results:

a. Improved Plow Steel. At the end of 10 weeks the unprotected bright wire rope was badly corroded with extensive general corrosion. Many of the individual wires in the strands had been completely severed by localized attack. Due to these "fishhook" type breaks and the extensive general corrosion, the rope would have no longer supported a useful load.

In contrast the cathodically protected bright wire rope was in decidedly better condition. The first 200 feet of the rope showed no more than slight general corrosion and there were no broken individual wires. At 208 feet the first fishhook was found, but there was still only a slight general corrosion. At the end of the rope, i.e., 427 feet from the anode, general corrosion was still quite limited

but numerous fishhooks were found. The broken individual wires were confined to the outer layer and constituted a small enough percentage of the total number of wires so that a moderately loaded structure supported by the rope would have maintained its structural integrity.

b. Galvanized Wire Rope. The unprotected galvanized wire rope after 10 weeks showed considerable general corrosion, but in contrast to the unprotected bright rope, there were no broken individual wires or fishhooks. There was also no corrosion evident on the 450 foot-length of cathodically protected galvanized rope at the end of 10 weeks.

At the end of 29 weeks, the cathodically protected galvanized rope has begun to show evidence of corrosion. The galvanizing has been maintained to a distance of 110 feet from the anode. Corrosion has been completely prevented for an addition 65 feet, but the galvanizing has been lost and the rope has assumed a dull black appearance. At a distance of 250 feet from the anode spots of light red rust have begun to appear, and at 320 feet about 40% of the surface is covered with light red rust. Examination of the bitter end of the rope at 450 feet revealed no fishhooks but severe local corrosion had taken place and the wire rope while still usable, has been greatly weakened.

c. Monel Rope. After 29 weeks the first 250 feet of monel rope under cathodic protection has not corroded. At about 300 feet, green corrosion products may be observed in crevices in the rope, and gradually increase in quantity towards the end of the rope. No broken wires have been observed, but moderately severe general corrosion has occurred at the end of the rope. The unprotected monel specimen showed evidence of severe general corrosion at 29 weeks.

d. Stainless Steel Rope. The cathodically protected stainless steel rope has exhibited no visible general corrosion after 29 weeks. However, detailed examination of the end of the rope revealed numerous fishhooks and crevices. The length of rope which was effectively protected is not known at present. As well as can be estimated from visual examination of the anode, the current required to maintain cathodic protection on the stainless steel rope has been less than for any of the other materials.

4. Summary and Conclusions:

The present admittedly limited data indicate that regardless of the type wire rope used, cathodic protection is required either to extend their life per se or to eliminate specific types of corrosion which are characteristic for the various materials. Based on these relatively

short term tests, cathodically protected galvanized wire rope would seem to be an attractive system for a low cost limited life system. The rope used in the experiment had very fine individual wires and an extremely thin galvanized coating. It could be anticipated that cathodically protected galvanized wire rope, with larger wire diameter and a much heavier galvanized coating which is available on heavier rope, would give a greatly extended life.

The monel rope with its high initial cost, low strength to weight ratio, and lack of immunity to corrosion under these conditions would not seem very attractive for marine use in submerged systems. Additional long term tests would, however, be required to definitely establish this item.

If the experience with the 304 stainless steel under cathodic protection is verified by further experiments, the use of cathodic protection in conjunction with stainless steel rope would seem to be one means of obtaining a reliable, long-life wire rope system in sea water. This would be especially true in instances where the initial cost of the stainless steel rope is not prohibitive. Further experimentation will be needed to determine the maximum length of stainless steel rope of various diameters which can be protected from one anode. Stainless steel would be of interest only if the anode spacing can be

significantly greater than for bright steel. In instances where it would not be impractical to have rather closely spaced galvanic anodes, the use of bright improved plow steel may be advisable.

II. STRESS CORROSION STUDIES

Prepared by L. J. Waldron

WW 041, [R05-24F]

A. GENERAL

The development of high-strength low alloy and maraging steels has opened up possible Naval applications of these materials where extreme strength is required as in deep diving submarines and other types of submersibles. It is important to know whether these materials will be susceptible in sea water to hydrogen embrittlement, stress corrosion, or cathodic currents as might be encountered in cathodic protection.

Facilities were available at the NRL Corrosion Laboratory in the Panama Canal for conducting such studies on these materials. A laboratory was set up at Fort Amador on the Pacific side. Seawater was pumped via a plastic pump and line from a pier in Panama Bay to a plastic tank located in a nearby laboratory. From here it was fed to the plastic cell surrounding the stressed samples and thence to a drain. No metal contacted the seawater from the time it was pumped from the ocean until it reached the stressed metal specimens. Thus the sea water was free of known contaminants. No attempt was made to control the temperature of the water flowing in the cells and it varied from 77° to 82°F.

The specimens used in these studies were a circular-notched tensile bar with a barrel diameter of 0.25 inches and approximately 2-1/4 inches in length. Each specimen had a 60° machined notch with a 1-mil root radius; the root diameter was 0.175 inches.

All specimens were stressed in tension to a value of 100,000 psi nominal (calculated on the root diameter) by a turnbuckle arrangement in an elastic alloy-steel ring (Fig. II-A-1). The barrels of the specimens were surrounded by a methyl-methacrylate cell through which the seawater flowed. Specimens were thoroughly degreased prior to being placed in the rings. They were then stressed to the selected values and the cells installed around the specimens. When a specimen broke it opened a clock circuit to register the time for rupture.

The specimens were tested in seawater uncoupled (i.e., freely corroding), coupled to zinc and magnesium, and made an anode when coupled to bronze. In some cases a battery and variable resistor were inserted in the circuit between specimen and anode or cathode to increase or decrease the current over that normally produced. In specific instances a few specimens were also stressed at 150,000 psi to determine the effect of increased stress.

The following materials were tested:

1. H-11 steel
2. 4340 steel
3. Eight experimental maraging steels.

Results of tests on the individual steels are discussed below.

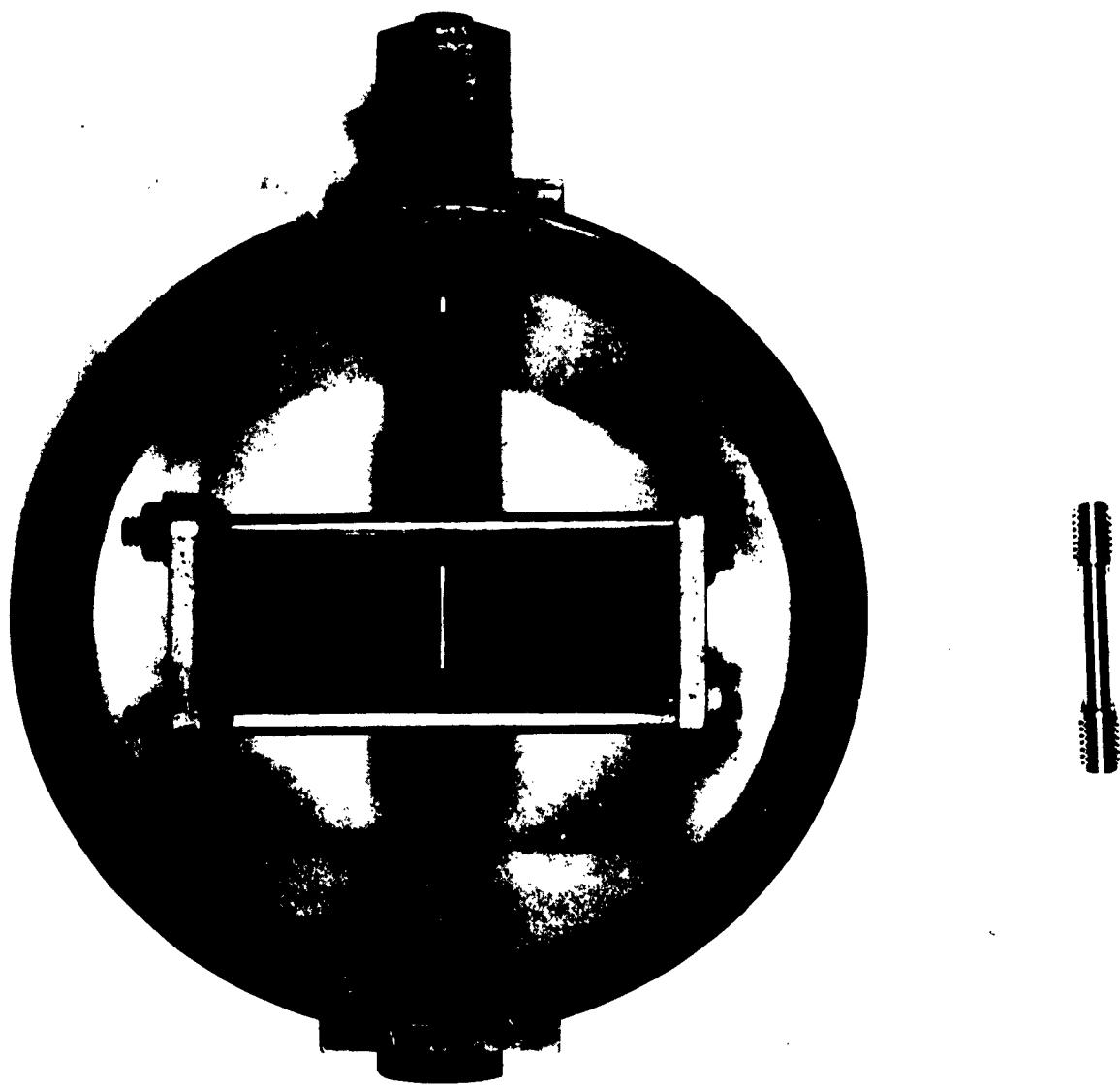


Figure II-A-1

B. EFFECT OF ELECTROCHEMICAL POTENTIAL ON THE CRACKING OF HIGH-STRENGTH H-11 STEEL

The alloy die steel designated AISI H-11 can be readily heat treated to a yield strength of 225,000 psi which (disregarding for the moment other properties) makes the steel attractive for various structural purposes, particularly for applications which place a premium on strength-weight ratio. It has even been suggested as a possible material for a simple deep-sea submersible, though it has long been known to be susceptible to stress-corrosion cracking. From many studies in the past, in various laboratories, it was known that some cathodic current could delay cracking but that excessive cathodic current caused rapid cracking from hydrogen embrittlement. These studies were all based on control of current rather than of potential. It was not clear whether potential control could afford a means to use H-11 safely in seawater.

This steel was stressed in tension as described in the general section of this report. The potentials of the specimens were controlled by either zinc or magnesium anodes operating through a manually-controlled variable resistor to give the desired potential. A silver-silver chloride half-cell was used as the reference electrode.

The findings for this series of experiments are summarized in Fig. II-B-1. These data indicate that

a small degree of cathodic polarization greatly increases the specimen life, but excessive potentials cause early failure from hydrogen embrittlement. There are three points of interest about the central area of Fig. II-B-1 and they are discussed below:

1. The potential range for extended life is fairly narrow if one is considering controlling the potential of a large and complicated structure. One is also not even certain that the curves defining the central area extend out to indefinitely long times (in terms of the anticipated service life of marine structures).

2. One of the simplest and most practical ways of being sure that all parts of a large and complex structure are cathodically protected at the same potential is to flame spray the surface with zinc. This, however, would move the potential away from the preferred central zone of Fig. II-B-1, i.e., to a point just to the right of -1.00 volts and would lead to rapid cracking from hydrogen embrittlement. In other words, the most reliable and practical method of controlling the potential (i.e., with a metallic zinc coating) would be to maintain the potential at such a negative value that susceptibility to hydrogen embrittlement may be encountered.

3. Even with the simple geometry and small size of the specimens used in these tests, some subtle change

can cause a specimen potentiostatted to the middle of the potential zone to experience premature failure.

These findings indicate that AISI H-11 steel at the strength level studied is not a practicable material for service in a marine environment either with or without cathodic protection. Under such circumstances it could only be used with a barrier coating having special but as yet incompletely defined properties. Such a coating would, in effect, separate the steel from the marine environment.

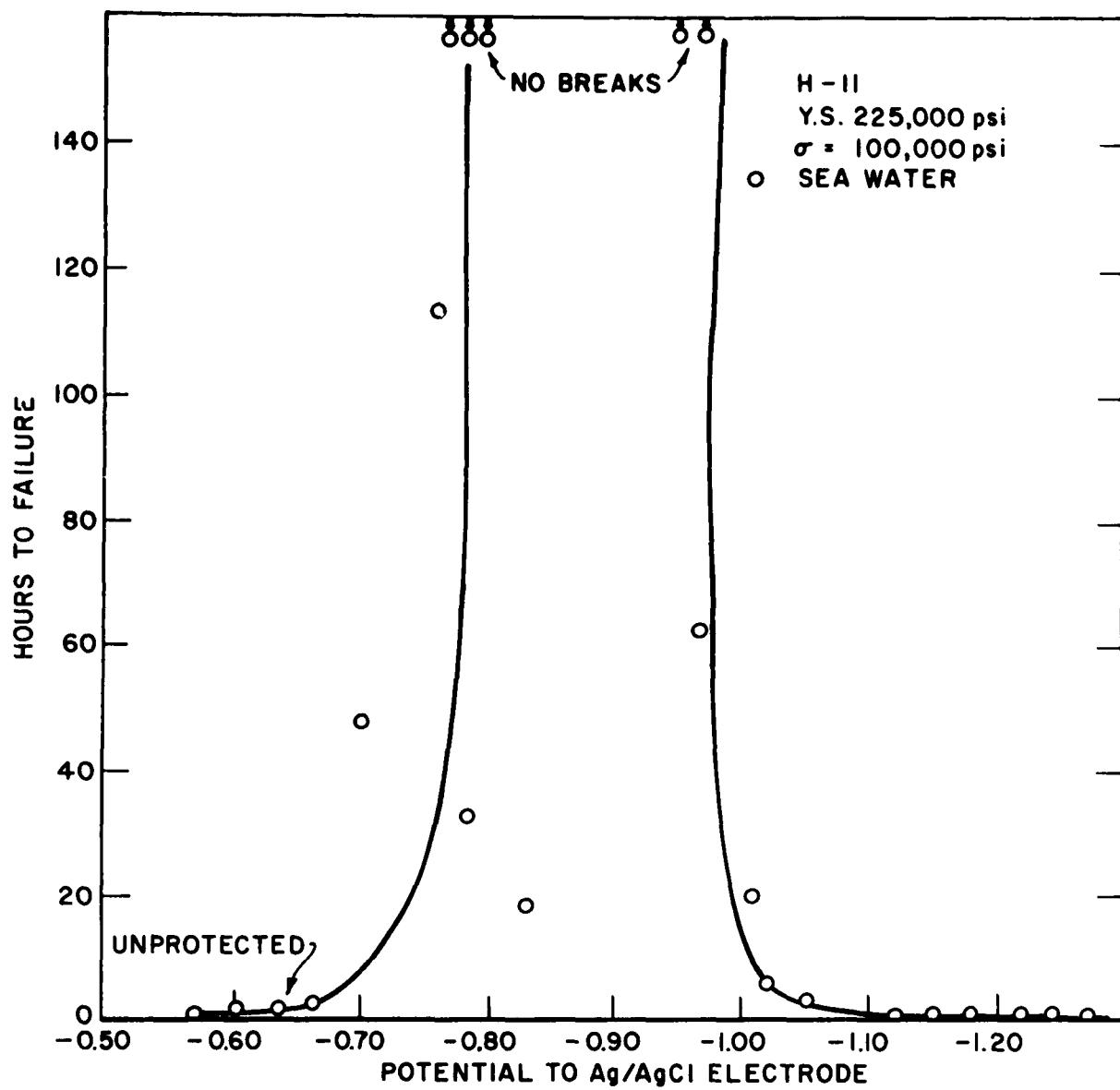


Figure II-B-1

C. 4340 STEEL

A limited number of specimens of 4340 heat treated to various yield strengths were available and stress corrosion studies were conducted at the Panama Laboratory. These were studied in tests as discussed in the General Section above.

Specimens of the 4340 steel were austenitized (30 minutes at 1550°F in argon), air cooled, triple tempered (2+2+2 hours); at each of the following temperatures 400°, 600°, 850°, and 1200°F. This should have produced yield strengths of 240,000 psi at the lowest tempering temperature and 130,000 psi at the highest tempering temperature.

Table II-C-1 gives a general summary of the results obtained.

Conclusions that can be tentatively drawn from these preliminary studies are as follows:

1. The specimens of higher yield strength, i.e., materials tempered at 400° and 600°F, in general were susceptible to both stress corrosion and hydrogen embrittlement.

From the specific data obtained on actual failures, the application of cathodic currents appears to have reduced the tendency of these materials to break from stress corrosion. The data on effect of cathodic currents are not nearly as conclusive, however, as those in Fig. II-B-1 for H-11 steel. A general statement is, therefore, not possible at

this time. When the specimens were coupled to magnesium, however, they readily failed from hydrogen embrittlement. No significant increase in the life of these high yield strength materials is believed possible by the application of cathodic currents but further work will be necessary to prove or disprove this item.

2. Material tempered at a higher temperature (850 and 1200°F - lower yield strength) did not break under any conditions of the test.

TABLE II-C-1

4340 STEEL
SUSCEPTIBILITY TO STRESS CORROSION CRACKING AND HYDROGEN
EMBRITTLEMENT

Triple Temper F	Uncoupled	Coupled to			Coupled as an Anode
		Zn	Carbon Steel	Mg	
400	0	X	0	0	0
600	X	0	0	0	0
850	X	X	X	X	X
1200	X	X	X	X	X

Note: 0 = broke
X - did not break

D. MARAGING STEEL

Samples from eight experimental maraging steels from another investigation were available for these studies. These steels had yield strengths of 140,000 to 280,000 psi. A limited number of circular notched specimens, as previously described, were machined from each of the eight materials. Studies on these materials were also similar to those described in the General Section of this report.

The results obtained with all specimens of the eight types of maraging steels are shown in Table II-D-1. While too many variables were present in these tests and an insufficient number of samples are available to allow one to draw definite conclusions, certain characteristic tendencies were noted and they are discussed below:

1. The 18% nickel-cobalt-molybdenum steels (highest yield strength materials) were all found to be susceptible to hydrogen embrittlement. This was shown by the fact that they broke when coupled to magnesium. Only the highest yield strength material was also susceptible to stress corrosion in flowing seawater. It also broke when coupled to a zinc anode which would indicate that it is quite sensitive to cathodic currents. Specimens of all eight materials broke under some conditions of exposure although in some instances both high stress and high cathodic currents were required.

2. In general, the susceptibility for a given material to break under an increasing number of conditions increased as the yield strength of the material increased.

3. Generally the materials tested were not stress sensitive. If a given material broke under one condition of test, it would also break under the same conditions at a different stress. This was especially true in the lower yield strength 12% nickel-containing maraging steels.

4. Undoubtedly, several factors characteristic of each material were responsible for the results observed. These had to do with the alloy composition, thermal history of the heats, mechanical handling during manufacture, etc.

In future studies these items should perhaps be given more careful consideration. This may assist in eliminating some of the scatter of results in individual tests as observed in this investigation. Incidentally, scatter of results have generally been indicated in stress corrosion cracking studies reported by others.

5. It is interesting to note that of 144 specimens tested under all the various conditions, 33% of them broke within 20 hours of testing, and 37% did not break after 100 hours. In other words, if a sample was susceptible to a specific test condition, it tended to break after a short period of stressing. If the specimen survived this period, it tended to remain unbroken for the entire test period. It

was either susceptible or unsusceptible to the given test condition with little chance for a half-way behavior. Of 61 samples that broke, 77% did so within a 20-hour period.

* * *

The question of test methods and concepts for the evaluation of the susceptibility of high strength steels to stress corrosion cracking and to hydrogen embrittlement is being examined before conducting any further evaluations.

TABLE III-D-1
MARAGING STEELS
SUSCEPTIBILITY TO STRESS CORROSION CRACKING AND HYDROGEN EMBRITTLEMENT

Sample Number and Nominal Composition	Stressed at 100K Coupled						Stressed at 150K Coupled					
	Yield Strength (K)	Stress % Yield	Uncoupled	to Mg*			to Mg†			Stress % Yield	to Mg‡ w/High Current	to Mg‡ w/Low Current
				Anode	Zinc	Mg	Anode	Zinc	Mg			
* 58 12Ni-3Cr-3Mo	152	66	X	X	X	X	0	0	0	0	99	0
* 83 10Ni-5Cr-3Mo	154	65	X	X	X	X	0	0	X	98	X	0
* 55 12Ni-5Cr-3Mo	162	62	X	0	0	0	NT	0	0	93	0	0
* 59 18Ni-9Co-3Mo	201	50	X	X	X	X	0	0	X	75	0	NT
* 63 18Ni-5Co-4Mo	220	45	X	0	X	0	0	0	X	69	NT	NT
* 84 18Ni-8Co-5Mo	260	38	X	X	X	X	0	0	X	58	NT	NT
* 57 18Ni-9Co-5Mo	280	36	0	0	0	0	NT	NT	NT	54	NT	NT

- * - battery included in circuit
- * - added resistance in circuit
- X - did not break
- O - broke
- NT - not tested

III. POTENTIODYNAMIC STUDIES

Prepared by J. A. Smith

RR 007-08-44-5510

A. POTENTIODYNAMIC INVESTIGATIONS OF PITTING PHENOMENA IN STAINLESS STEELS

1. Introduction

The comparative inertness of the stainless steels to attack by many aqueous electrolytes is directly attributable to their ability to form minutely soluble, pore-free oxide layers. These layers prevent direct contact of the aqueous electrolyte with the bare metal.

The introduction of halogen anions such as Cl^- causes the partial or total breakdown of these oxide layers. Two distinct electrochemical phenomena occur in this instance. One phenomenon is described as the breakdown potential, E_r , and corresponds to the rupture of the oxide layer. The actual breakdown potential is the value at which a sharp break occurs in the anodic polarization curve. The second phenomenon is described as the oxide film repair or protective potential, E_p , and corresponds to the potential value at zero current flow when the impressed potential is being varied in the noble direction.

A convenient method to obtain the potential values E_r and E_p is the potentiodynamic technique. In this method the metal being investigated is made an electrode in an electrochemical cell and is then polarized potentiostatically

either anodically or cathodically between selected potential values.

2. Experimental Details

The electrodes were fabricated from commercially available rod stock and, except for Types 316 and 410 stainless steel, were 1/4-inch in diameter. The 316 and 410 stainless steel were 3/8-inch in diameter. The electrodes were metallographically prepared by emery grinding and a final polishing with an Al_2O_3 impregnated billard cloth covered wheel.

All chemicals used in the preparation of the solutions for these studies were reagent grade.

The potentiostat utilized (manufactured by a division of one of the oil companies) had the following characteristics: potential setting, ± 1 mv and a minimum potential sweep rate of 1.6 volts per hour. Fig. III-A-1 shows the cell and accompanying apparatus.

The potential-current curves were obtained under conditions of continuous de-aeration. A sweep rate of 1.6 volts per hour was used in determining the anodic to cathodic and cathodic to anodic potential curves. Experiments were conducted on a series of stainless steels in a 0.10M NaHCO_3 solution containing 0.005M, 0.05M, and 0.6M NaCl .

3. Summary and Results

The breakdown potential, E_r , was taken as that potential corresponding to a marked increase in anodic current when the potential sweep was from the cathodic to anodic direction. The protective potential, E_p , was taken as that potential value where the potential-current curves cross the zero current axis when the potential sweep was from the anodic to cathodic direction. The values E_r and E_p for 304 stainless steel in the 0.1M bicarbonate solution containing 0.05M NaCl are shown in Fig. III-A-2.

In Figs. III-A-3 and III-A-4 the values of E_r and E_p are plotted respectively as a function of NaCl concentration for 316, 304, 321, 347, and 410 stainless steels.

As would be expected, the effect of chloride ion upon the breakdown potential varies with the composition of the stainless steel. For the 0.10M NaHCO_3 plus 0.005M NaCl solution, the concentration of chloride ion was apparently too low to appreciably effect the breakdown potential of the oxide layer. In this solution the integrity of the oxide layer was almost entirely dependent on the imposed potential, and it is not unreasonable to find the breakdown potentials of the entire series clustered around a single value of 870 millivolts to the saturated calomel reference electrode.

As the chloride concentration was increased to 0.05M or 0.6M, the effect of the chloride ion became evident. The

most anodic breakdown potential was found for 316 stainless steel, with the breakdown potentials becoming increasingly anodic for 304, 321, and 347 stainless steel. The breakdown potential of 410 stainless steel was less anodic than any of the other steels studied.

In the case of the film repair or protective potentials, E_p , both stainless steel composition and chloride ion composition have an effect. The steel composition effect is evident since the E_p values representative of the various stainless steels varied at specific chloride ion concentrations.

The oxide layers on 316, 304, and 321 stainless steel are of such a nature, however, that the protective potential, E_p , is nearly identical to the film rupture potential, E_r , in the solution containing the lowest chloride ion concentration. In contrast the oxide layers on 347 and 410 stainless steel are not repaired at the rupture potential, i.e., E_p is more noble than E_r as the level of anodic polarization is decreased. This would indicate that once corrosion had begun on the latter two materials, it would continue until their more noble protective potential, E_p , is reached.

The effect of chloride ion concentration on the film repair or protective potential, E_p , is evident in the solutions containing 0.05M and 0.6M chloride ion. In these more concentrated solutions the protective potentials, E_p , of all the stainless steel studied were more noble than the

film repair potentials, E_r . One would, therefore, expect that all of the stainless steels studied would be subject to pitting attack in the 0.1M NaHCO_3 solution when the chloride ion concentration was either 0.05 or 0.6M.

4. Conclusions

From this data it would be predicted that: 410 stainless steel has the greatest sensitivity to pitting attack, with 347, 321, 304, and 316 stainless steel possessing progressively less sensitivity to pitting attack.

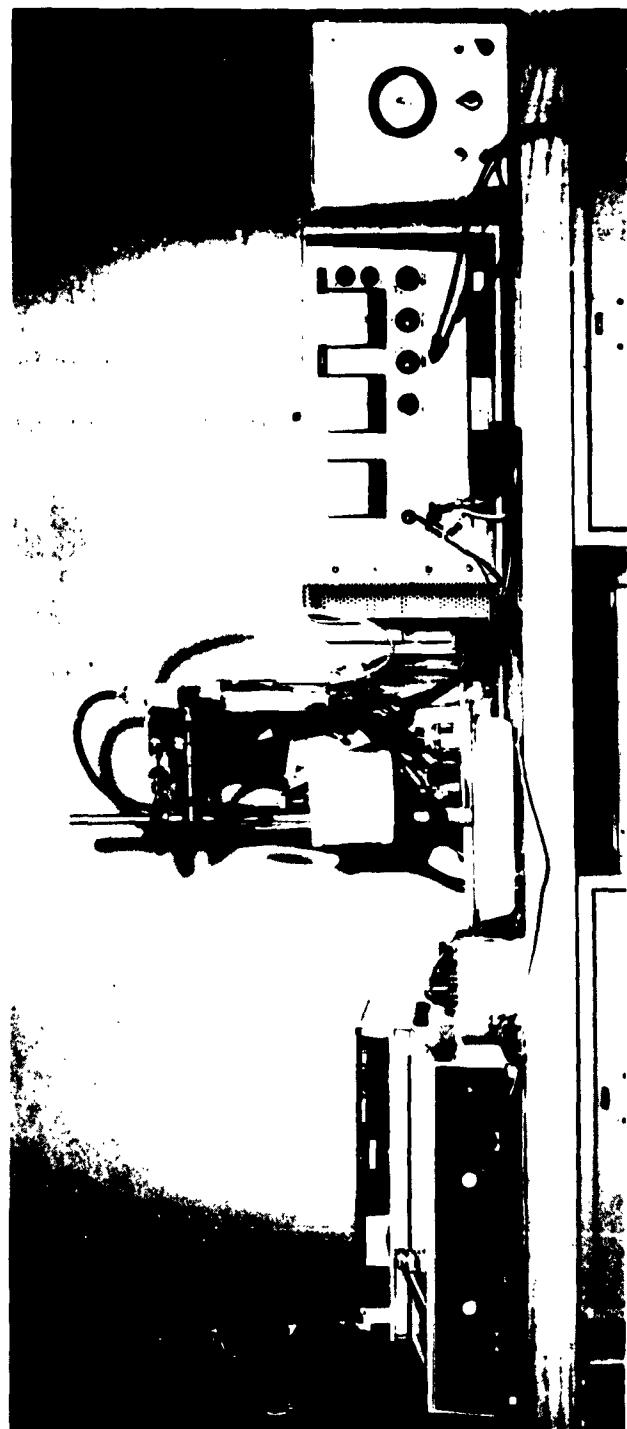


Fig. III-A-1 - Potentiodynamic studies experimental apparatus

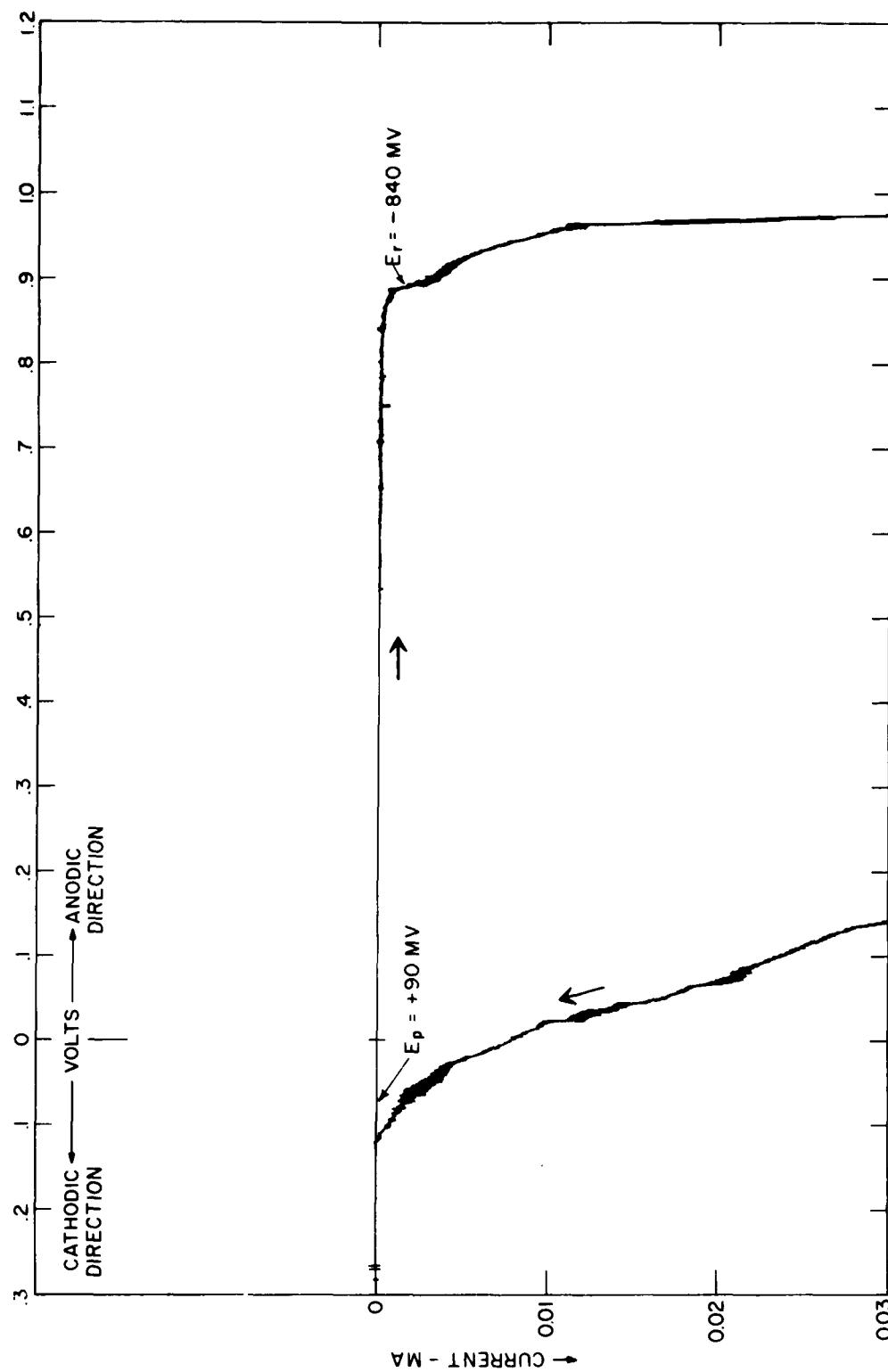


Fig. III-A-2 - 304 stainless steel. Solution 0.10 M NaHCO_3 + 0.05 M NaCl.

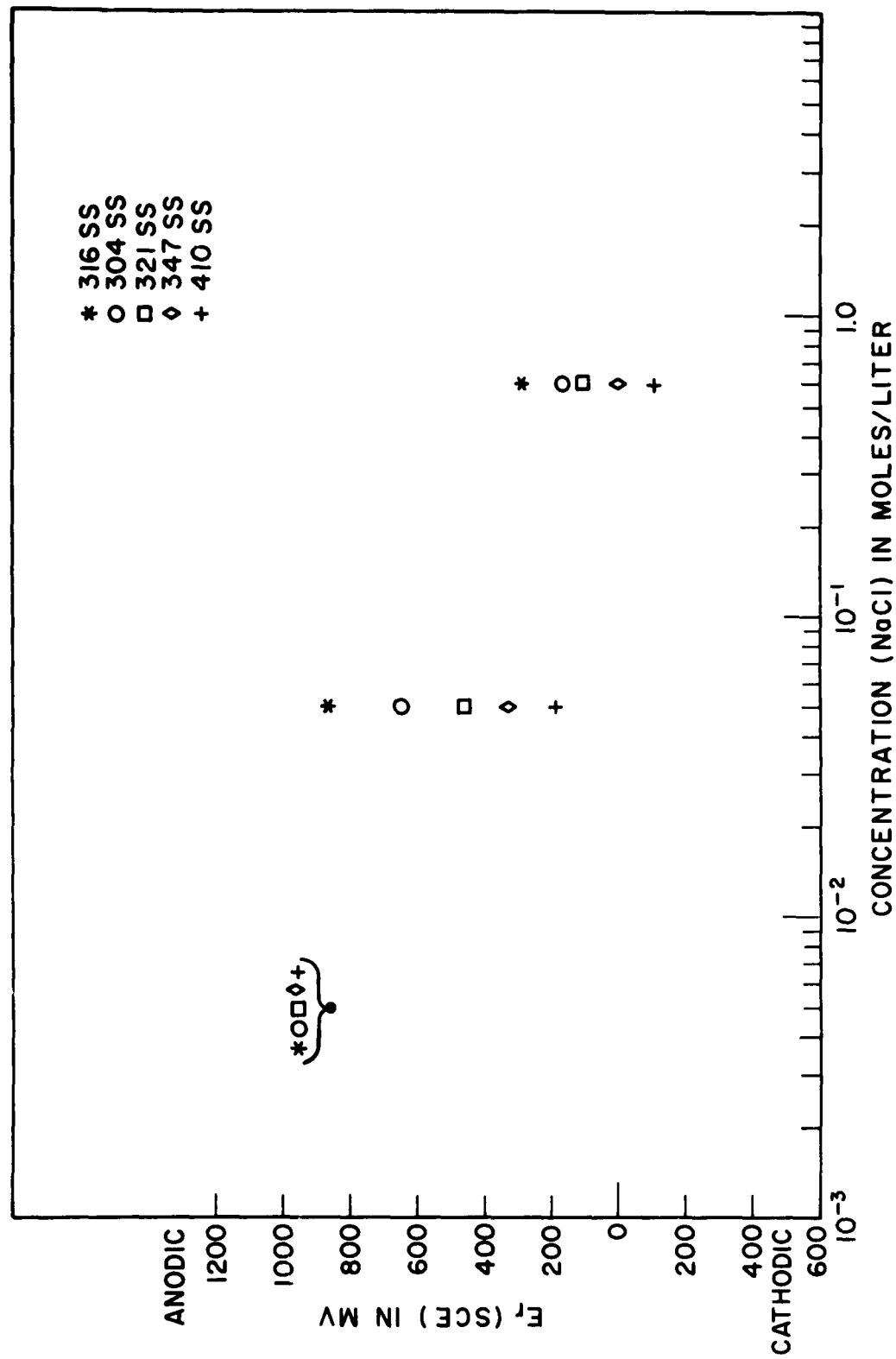


Fig. III-A-3 - Breakdown Potentials (E_r) of the oxide layer on stainless steels at 25°C in solutions of 0.10 M NaHCO_3 containing chloride

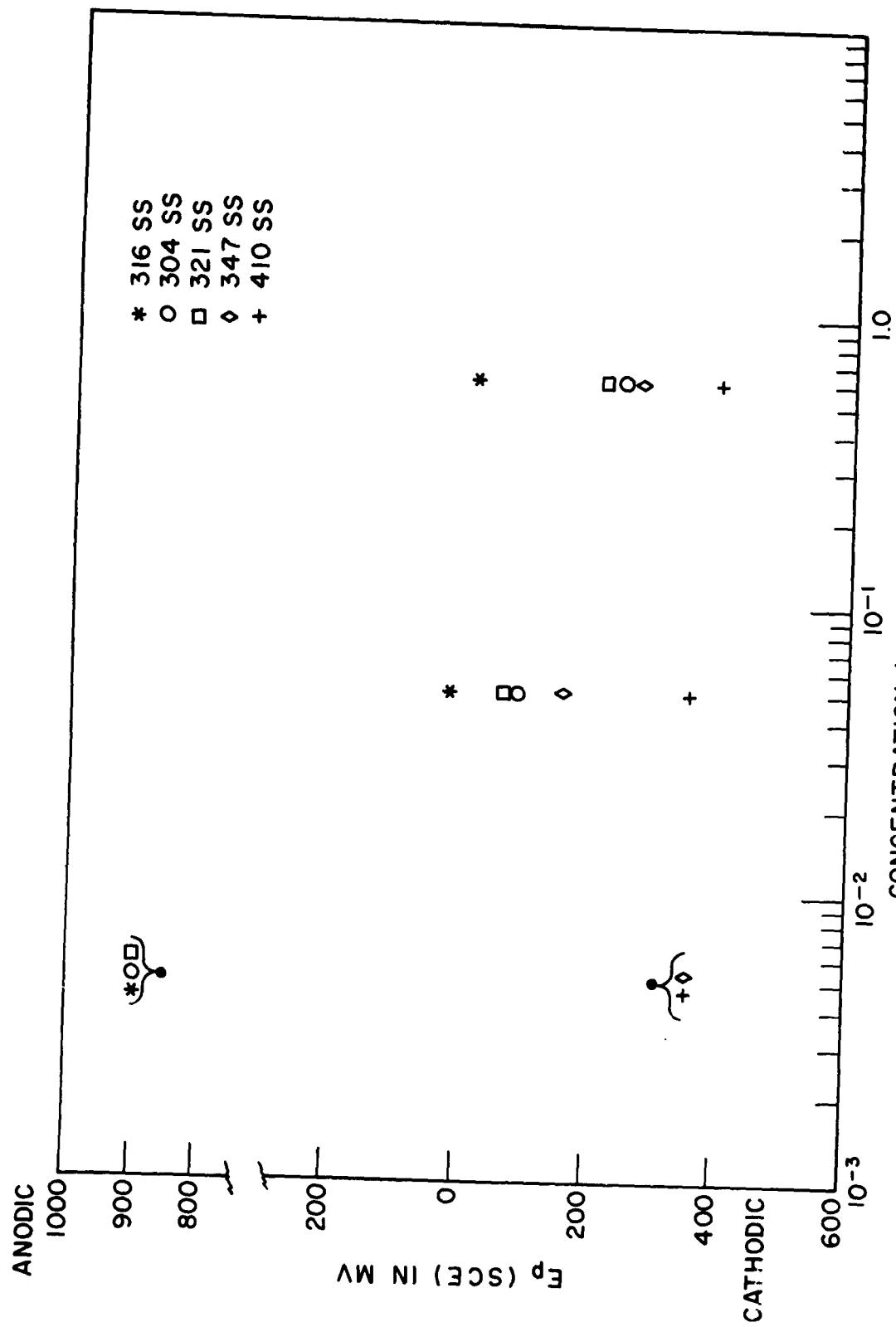


Fig. III-A-4 - Protective potentials (E_p) of some stainless steels at 25°C in solutions of 0.10 M NaHCO₃ containing chloride

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